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Robert A. Taft Sanitary Engineering Center
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INTRODUCTION

Plastic bags have excellent possibilities for the storage of inorganic and organic gases and vapors. Recently, several types of plastic materials have been evaluated for use as containers for low concentrations of various chemical species. Baker and Doerr (1959) studied the storage over 17 to 67 hour periods of 30 to 130 ppm of ethylene, 1-pentene, 2-methylpentane, benzene, acetone, butyraldehyde, sulfur dioxide, and nitrogen dioxide in "Mylar," aluminized "Mylar," "Saran," Scotchpak," and aluminized "Scotchpak" bags.* They concluded that the hydrocarbons, acetone, and butyraldehyde could be stored satisfactorily. Large losses of nitrogen dioxide and sulfur dioxide were observed during storage in plastic bags (Baker and Doerr, 1959). Wilson and Buchberg (1958) found that nitrogen dioxide at 1 ppm was stable in "Kel-F" bags up to 120 hours, but observed serious losses of nitrogen dioxide in polyethylene bags after 5 hours. Losses of acetone at 2 and 4 ppm in a polyethylene bag also were reported (Wilson and Buchberg, 1958).

Since plastic bags have considerable advantages over rigid containers, "Mylar" and aluminized "Scotchpak" bags have been used in

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* Trade names are used for identification purposes only and not to imply endorsement by the Public Health Service.

our laboratory for several years. Such bags are light, inexpensive, and no dilution corrections are necessary when emptying them. However, plastic bags must not be used indiscriminately. For many gases and vapors, one or another plastic material provides an excellent container. Slow but acceptable losses of some other chemical species occur in the bag. Some substances in certain plastic bags will be lost rapidly. The rate of loss is a function of the type of gas or vapor, its concentration, and the type of plastic material used for the container. It also is absolutely essential to realize that an individual substance in air at ambient temperature may be quite stable in a plastic bag, while the same substance in combustion products cooled to room temperature in the bag may be lost rapidly owing to its interaction with water vapor and reactive chemical species in the combustion gases. Consequently, generalization is dangerous and data are necessary for each type of chemical compound in a specific plastic bag in a variety of gas mixtures. Only in this way can the possibilities and limitations of such containers be properly defined.

It should be always kept in mind that no container can prevent gas phase reactions from resulting in losses of starting materials. Furthermore, if the sample is initially saturated with water vapor, condensation of the water will remove soluble chemical species such as nitrogen dioxide or formaldehyde very readily. Once a film or a liquid deposit is formed, even within a bag made of quite inert material, it will prove very difficult ever to recover for subsequent analysis the materials dissolved in the film or condensate.

In various investigations in our laboratory considerable data have been obtained on a number of substances in the 0.1 to 1000 ppm

range stored for several hours to several days in "Mylar" and "Scotchpak" bags. The compounds investigated most include numerous olefins, formaldehyde, acrolein, ozone, nitrogen dioxide, and sulfur dioxide. Many other substances, including aromatic hydrocarbons, phenols, crotonaldehyde, and alcohols, have been used in these bags but only qualitative or semi-quantitative information was obtained on their stability. Data also have been obtained on the stability of olefins, formaldehyde, acrolein, and nitrogen dioxide in samples of automobile exhaust effluents and diluted irradiated automobile exhaust stored in plastic bags.

EXPERIMENTAL DETAILS

The stability of ozone and nitrogen dioxide was determined using a coulometric ozone sensor produced by Mast Development Co., Davenport, Iowa (Wartburg, Brewer, Lodge, 1960; Altshuller and Wartburg, 1961). The olefins were determined by a colorimetric method (Altshuller and Sleva, 1961) and a coulometric instrument also produced by Mast Development Co., Davenport, Iowa (Nicksic, 1960). The formaldehyde was determined by the chromotropic acid procedures (West and Sen, 1956; Altshuller, Miller, and Sleva, 1961). Acrolein was measured by the colorimetric 4-hexylresorcinol method investigated by Cohen and Altshuller (1961). Sulfur dioxide concentrations were obtained by the colorimetric method of West and Gaeke (1956).

The aluminized "Scotchpak" used was obtained from Minnesota Mining and Manufacturing Co., St. Paul 6, Minnesota. This material can be easily heat sealed to give an inexpensive plastic container. The "Mylar" bags used were obtained from Schjeldahl Co., Northfield, Minnesota.

RESULTS

Results were obtained for different types of gaseous and vapor mixtures. The synthetic mixtures consist of individual chemical species or mixtures of these compounds diluted with air to the 0.1 to 1000 part per million range. The term raw automobile exhaust refers to exhaust gases sampled directly from the exhaust system of an automobile being cycled through a set of cruise and deceleration cycles on a chassis dynamometer. Diluted automobile exhaust refers to automobile exhaust proportioned representatively and diluted with a 100- to 1000-fold excess of purified air. Diluted irradiated exhaust refers to the same diluted exhaust irradiated with banks of fluorescent lamps as it flows through a large aluminum and "Mylar" chamber. The average irradiation times were one to two hours.

Olefins. - A mixture containing 12 ppm of trans-2-butene in air was prepared in an aluminized "Scotchpak" bag and the olefin concentration determined colorimetrically (Altshuller and Sleva, 1961) several times during an 18 hour storage period. A 7% to 8% decrease in concentration was observed. Numerous analyses made on a number of individual four, five, and six carbon olefins and on olefin mixtures in both aluminized "Scotchpak" and "Mylar" bags showed no measurable decrease in concentration during two to four hour storage periods. Colorimetric determinations on diluted and diluted irradiated automobile exhaust also showed no significant loss of olefins in "Scotchpak" bags during several hours. A 15% to 20% loss of olefins from a sample of automobile exhaust was observed in 18 hours. Chemical reaction in the gas phase probably was responsible for part of this loss.

The results obtained by the colorimetric method on synthetic systems were confirmed by use of a continuous monitoring olefin instrument. Olefin losses of no more than 5% to 10% occurred in 24 hours. These results were observed for mixtures containing 20 to 400 ppm of 1-butene, trans-2-butene, or 1,3-butadiene in air in "Mylar" and aluminized "Scotchpak" bags.

Formaldehyde. - Losses of formaldehyde can occur quite readily in the plastic bags used in the present work. When a synthetic mixture containing a few parts per million of formaldehyde in air was analyzed in an aluminized "Scotchpak" bag, a 10% loss of formaldehyde occurred in three hours and a 25% loss in 22 hours of storage. However, a similar formaldehyde in air mixture in a "Mylar" bag showed less than a 5% loss of formaldehyde in 24 hours.

Larger losses of formaldehyde do occur during storage in "Mylar" bags (Altshuller, Cohen, Meyer, and Wartburg, 1961) of diluted, irradiated automobile exhaust. Samples of irradiated exhaust containing formaldehyde in the same concentration range as the synthetic mixture, two to three ppm, showed 5% to 10% formaldehyde losses in about two hours in "Mylar" bags. No formaldehyde could be detected in an aluminized "Scotchpak" bag containing raw automobile exhaust. Samples collected in evacuated glass flasks containing aqueous collection solutions analyzed at just under 30 ppm of formaldehyde. However, with raw automobile exhaust, no formaldehyde can be detected even when collection is made into dry glass flasks (Altshuller, Cohen, Meyer, and Wartburg, 1961). The severe losses of formaldehyde from raw exhaust are probably due largely to the carriage of the formaldehyde to the walls with the water vapor and condensate.

Acrolein. - Acrolein is much more stable in aluminized "Scotchpak" or "Mylar" bags than formaldehyde. Samples of raw automobile exhaust show less than 10% losses of acrolein in aluminized "Scotchpak" bags after 24 hours. During 48 to 72 hours of storage appreciable losses of acrolein do occur. Synthetic acrolein-in-air mixtures in the 0.1 to 10 ppm range are extremely stable.

The acrolein lost to the surface of the plastic bags will be partially desorbed back into the gas phase. Several series of runs were made with plastic bags whose surfaces had been in contact for as long as several hundred hours with synthetic vapor samples containing acrolein. These bags had been flushed with clean air many times over this period. The bags were filled with clean air and air samples were withdrawn and analyzed colorimetrically (Cohen and Altshuller, 1961) after periods ranging from a few hours to several days. The results indicated that 3% to 5% of the original concentration of acrolein used was attained at equilibrium. For example, if a bag had been used for the analysis of synthetic samples of 10 pphm of acrolein in air, the residual acrolein concentration found would be from 0.3 to 0.5 pphm. Similar results were obtained with a bag which had been used for the collection of raw automobile exhaust. The equilibrium residual acrolein concentrations appear to be attained after several hours. Repeated flushing with clean air will slowly reduce the residual acrolein concentration.

Ozone. - Ozone decomposes rapidly in aluminized "Scotchpak" bags. Only a slow loss of ozone occurred when a "Mylar" bag containing about 70 pphm of ozone was monitored with an ozone instrument for five hours; about a 10% loss of ozone was observed. In a 16-hour "Mylar" bag test a

decrease in ozone concentration from 90 to 55 pphm was measured, indicating about a 40% loss of ozone. Part of this loss is due to the large increase in surface to volume ratio as the b g is nearly depleted increasing the rate of ozone decomposition. Consequently, a rate of loss of ozone of about 2% to 3% per hour probably occurs. In measurements made over one or two hours such a small loss is hardly measurable compared with the noise level and drift of the instrument. The stability of ozone stored in other types of containers has been investigated (Wilson and Buchberg, 1958; Baker and Doerr, 1959). Losses of ozone on plastic and metallic tubing materials also has been studied (Altshuller and Wartburg, 1961).

Nitrogen Dioxide. - No significant decrease was observed in nitrogen dioxide at 0.2 to 5 ppm in "Mylar" bags over periods of a few hours. In eight hours a loss of about 5% of the nitrogen dioxide occurred. Over 48 hours a decrease of nitrogen dioxide concentration from 2.7 to 2.0 ppm was measured. Again this is partially due to increased surface to volume ratio as the bag collapses. Consequently, the rate of loss of nitrogen dioxide in synthetic mixture is only about 1% per hour in "Mylar" bags.

Measurements have been made on the nitrogen dioxide formed from the oxidation of 1000 ppm of nitric oxide in "Mylar" bags. In addition, the concentration of nitrogen dioxide in "Mylar" bags filled initially with 500 and 800 ppm of nitrogen dioxide was investigated. No significant losses of nitrogen dioxide were observed in these synthetic mixtures over three hour storage periods. Over 18 to 20 hours storage, about a 20% loss of nitrogen dioxide was observed.

Much greater losses of nitrogen dioxide might be expected in raw automobile exhaust samples. Automobile exhaust samples were collected

which contained total nitrogen oxide in the 500-1000 ppm range. Shortly after collection, an exhaust sample analyzed at 130 ppm nitrogen dioxide. Most of the nitric oxide should have been oxidized overnight to nitrogen dioxide by the residual oxygen. However, only 260 ppm of nitrogen dioxide was found in the bag after 22 hours. Appreciable losses of nitrogen dioxide to the walls probably occur. In analyses of acrolein in raw exhaust by the 4-hexylresorcinol method (Cohen and Altshuller, 1961) the nitrogen dioxide content can also be followed, owing to a nitrogen dioxide product absorption band in the ultraviolet. Using this band as an index of nitrogen dioxide content, almost complete loss of nitrogen dioxide from the gas phase in 24 hours in an aluminized "Scotchpak" bag is indicated. Actual attack of the nitrogen dioxide on the bag material can be seen as minute discolorations on the surface of the film.

Sulfur Dioxide. - Synthetic mixtures of sulfur dioxide in air can be stored in "Mylar" bags for a number of hours without significant losses. Hourly measurements for four hours gave sulfur dioxide content of 0.49, 0.50, 0.43, and 0.49 ppm respectively. In two hours with higher sulfur dioxide concentration, the sulfur dioxide content in the bag analyzed at 4.4, 5.0, and 4.8 ppm during this period. Serious losses of sulfur dioxide do occur over a period of two or three days.

Conditioning of the "Mylar" bag with sulfur dioxide is essential before actual use. Addition of a much higher content of sulfur dioxide than is needed, followed by repeated dilutions down to the desired concentration level, works satisfactorily.

DISCUSSION

The results given in this work indicate that the plastic materials used, particularly "Mylar," will permit the storage of many types of chemical species in synthetic mixtures for at least 24 hours. However, somewhat more rapid losses will be experienced from real samples of atmospheric gases containing highly reactive species such as formaldehyde. The loss of many chemical species from undiluted combustion source samples is likely to be serious. However, some species such as hydrocarbons and acrolein appear to be quite stable in combustion sources over periods of at least eight hours. Certainly, exceptions will occur even in the hydrocarbon series for highly reactive molecules such as 1,3-butadiene and for higher molecular weight hydrocarbons, perhaps those containing eight carbon atoms and above.

Large losses of many types of materials can be anticipated when new plastic bags are used. New bags should be filled and emptied several times with the selected type of sample, to condition them. The more drastic the losses experienced with conditioned bags, the more essential becomes conditioning of new bags. Consequently, it is necessary that new bags should be filled, allowed to stand in contact with combustion source samples, and emptied several times before the bag is actually used for a storage container.

The available data do not give information on very rapid initial losses which may occur within the few seconds or minutes after filling the bag. It is possible that the largest losses may occur rapidly and be followed by slow additional losses over a period of many hours. Rapid initial losses would appear to be more likely with a new bag rather than

a bag whose surface has been previously equilibrated with the chemical species of interest.

Very few data are available on the storage of substances in bags made out of fluorinated plastic materials. Wilson and Buchberg, 1959, did obtain data at rather high concentrations for pentane, cyclohexene, methanol, and acetone, and for nitrogen dioxide at 1 ppm which indicates excellent stability in "Kel-F" bags. Ozone has been shown to be quite stable when flowing through long lengths of Teflon tubing (Altshuller and Wartburg, 1961). Further investigation of the use of fluorinated plastic films as bag materials would be desirable.

The results available indicate that plastic bags serve as excellent reservoirs for synthetic mixtures to be used in the calibration of various instruments or chemical methods. Low concentrations of automobile exhaust diluted with air either before or after irradiation also appear fairly stable in plastic bags for limited periods of time. Samples collected directly from combustion sources present more of a problem. Bags of some plastic materials which have been properly conditioned probably are satisfactory containers for most of the hydrocarbon species and a limited number of other unreactive species found in combustion sources. Bags are likely to be unsatisfactory for many of the more reactive organic and inorganic species in combustion sources such as formaldehyde, nitrogen dioxide, and sulfur dioxide. However, further investigation is necessary to answer these questions.

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